

Surface Composition and Chemical State of Fe and Mo Impregnated Subbituminous Coal

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ABSTRACT

The surface composition and chemical states of elements in samples of Wyodak subbituminous coal impregnated with Fe and Mo were investigated. The concentrations of Fe, Mo, S, Al, Si, Ca, C, O, and N were determined by x-ray photoelectron spectroscopy (XPS) in samples impregnated with 0.7-2.0 wt% Fe and 500-1000 ppm Mo. The metals were deposited on the samples by an incipient wetness technique using solutions of ferric nitrate, ferric sulfate, ferrous sulfate and ammonium molybdate. The effect of the metal precursor, the relative amounts of Fe and Mo loading, the effect of base-treatment with NH_4OH and the chemical states of the elements are discussed. Deconvolution of the overlapped S_{2s} and Mo_{3d} peaks is described along with a brief overview of the liquefaction performance of these coals.

INTRODUCTION

Highly dispersed iron-based catalysts have been extensively studied for direct coal liquefaction during the last several years. Cugini and his workers[1,2] found that finely divided and highly dispersed FeOOH -impregnated coals prepared by an incipient wetness technique have high activity in direct liquefaction. These coals were prepared by impregnating the surface of the coal with a solution of ferric nitrate followed by precipitation of FeOOH using an excess of NH_4OH . The influence of several parameters in the preparation procedure on the surface chemistry and performance of the impregnated coals was previously reported.[3]

Considerable research has been directed toward exploiting the improved liquefaction performance of mixed Fe and Mo catalyst.[4,5] Garg, et al., found higher conversion and oil yields by simultaneously impregnating coal with 1% Fe and 0.02% Mo using solutions of 10% ferrous sulfate and 0.5% ammonium molybdate.[6] The iron sulfates are among the least expensive form of iron compounds that are available because of their abundance as a by-product from the iron and steel industry. Andres, et. al.,[7] prepared Mo-free impregnated coals using aqueous solutions of FeSO_4 and reported poor reproducibility of the impregnation technique and relatively low catalytic activity in liquefaction. Pradhan, et al.,[8] reported increased activity for direct liquefaction of subbituminous coal with sulfated α -hematites containing small amounts of added Mo.

Since Mo is expensive, its application in liquefaction will depend on maximizing activity at low concentrations while simplifying the preparation in order to minimize catalyst processing costs. In order to optimize the metal function, it is necessary to understand the surface chemistry of the catalytic components. The present study extends the investigation to coals impregnated with both ferric and ferrous sulfate and compares them with results previously reported using ferric nitrate. The effect of base precipitation and method of drying, whether in air or N_2 at atmospheric pressure or under vacuum, were determined for coals impregnated with 0.7-2.0 wt % Fe and 0.05-0.1 wt % Mo. The surface composition and chemical state of several surface elements were studied using XPS. The technique for measuring low concentrations of Mo by XPS is discussed.

EXPERIMENTAL

Materials - Reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ were purchased from Aldrich Chemical Co. and Wyodak coal from the Black Thunder Mine in Wright, Wyoming was provided by CONSOL, Inc. The ultimate analysis of the coal on a dry basis was as follows: carbon, 72.2%; hydrogen, 4.3%; nitrogen, 1.2%; sulfur, 0.5%; oxygen (by difference), 16.0%; ash, 5.8%.

Preparation of Impregnated Coals - Metal impregnated coal samples were prepared as described previously[3]. To as-received coal, which contained 21 wt% moisture, was added dropwise, while stirring, 0.25 ml per gram dry coal of ammonium molybdate solution followed by 0.5 ml per gram dry coal of aqueous Fe salt solution. For those samples treated with base, 1.54 M NH_4OH solution was added at an $\text{NH}_4\text{OH}/\text{Fe}$ mole ratio of 139 and filtered. In some cases samples were further washed with water. All were dried to a final moisture content of 3-10%.

XPS Analysis - XPS analyses were performed on a LHS-10 Leybold-Heraeus spectroscope

as described previously[3]. The quantification of elemental concentrations was performed using background subtraction and element sensitivity factors. Mo measurements were complicated by the overlap of the S_{2s} peak with the Mo_{3d} peaks. Reference samples containing sulfated iron oxides were used to determine the correct position and the area under the S_{2s} peak. Knowing the area of the S_{2p} peak and the S_{2s}/S_{2p} ratio, the S_{2s} peak area was calculated. Subtraction of the S_{2s} peak area from the Mo_{3d} peak area provided a measurement of the Mo concentration.

RESULTS AND DISCUSSION

The surface composition of coals impregnated with the Fe^{++} or Fe^{+++} sulfates are shown in Table 1 and compared with coal impregnated with $Fe(NO_3)_3$ and precipitated as $FeOOH$ by addition of NH_4OH (CH-31). The surface iron concentrations of the 0.77 wt% Fe-impregnated coals prepared from either Fe^{++} or Fe^{+++} sulfates were less than for the $Fe(NO_3)_3$ impregnated coal. For these same coals the sulfur concentrations on the surface are significantly less when base was used to precipitate the iron. Sulfate analysis of the NH_4OH filtrate from the base treatment of CH-51 indicated that all of the $SO_4^{=}$ ion had dissolved in the filtrate making the surface free of any sulfur and oxygen associated with the $SO_4^{=}$ ion. Although several of the NH_4OH preparations were further washed with water with the intention of removing sulfate, including CH-51, it was not necessary. The surface concentrations of Si and Al, and Ca for the 0.77 wt% Fe-impregnated coals, except for CH-502, decreased on the surface when base was used. There was no consistent bias from drying in air, nitrogen or under vacuum.

Surface concentrations of Fe-Mo impregnated coals are shown in Table 1. For those coals subjected to base precipitation (CH-6, CH-61), the Mo concentration is lower (CH-601, CH-604), presumably because part of the molybdate had partially dissolved in the NH_4OH solution. Coals impregnated with Mo at 500 (CH-61) and 1000 ppm (CH-6) had Mo concentrations on the surface of 1100 and 1400 ppm, respectively. For the non-base washed coals, to which 1000 ppm Mo was added, the final Mo levels were 3000 and 5100 ppm. The Fe concentrations of 2.3-3.0 wt% on Mo-impregnated coals were higher than for the Mo-free coals, but still tended to be lower than for the base-treated coals, of which CH-6 is at the lower end. The oxygen levels were slightly higher while the sulfur levels were significantly higher for the non-base treated samples indicating significant deposition of $SO_4^{=}$ on the surface relative to the $SO_4^{=}$ -free ferric nitrate impregnated coals. The rather narrow range of oxygen concentrations on the surface for these 0.77 wt% Fe-impregnated coals (23.1-26.6) suggest that oxygen concentration is related to the iron surface concentration. Like the Mo-free coals, the surface concentrations of Si and Al decreased for the NH_4OH treated coals. No difference in Ca concentration was observed. There didn't appear to be any significant differences in the surface compositions of the Fe^{+++} and Fe^{++} -impregnated coals, even though in the preparations the instability of the ferrous salt solution was obvious. The original blue-green color of the $FeSO_4$ solution rapidly changed to yellow upon exposure to air during the application step. A slight deposit of particles was found in the beaker.

Surface Chemistry - The binding energies of the various elements are shown in Table 2. For both the Fe- and Fe-Mo-impregnated coals treated with base, binding energies for $Fe_{2p\ 3/2}$ and Fe_{3p} were ≥ 711.1 eV and 56.0-56.6 eV, respectively. The O_{1s} binding energies for all the samples prepared with iron sulfates were ≥ 532.0 eV, except for the base-treated sample containing 2 wt% added Fe, CH-51. The $Fe(NO_3)_3$ impregnated coal had a lower O_{1s} binding energy (CH-31), which is consistent with the $FeOOH$ structure. The higher binding energies, reported previously for the raw coal and low Fe concentrations[3], indicate the dominance of the Si and Al oxide structures. The $Fe_{2p\ 3/2}$ peak for the non-base treated samples was broadened toward lower energy suggesting either more contribution from FeO , Fe_3O_4 , or Fe_2O_3 type structure. Low-intensity peaks were observed in the sulfur region at 169.0-169.7 eV, specifically for the base-treated samples, and much more intense peaks were observed between 170.9-171.5 eV for the non-base treated samples. The latter are related to the abundance of $SO_4^{=}$ species present in the samples while the lower energy peaks are related to the background mineral sulfur content of the coal.

The $Ca_{2p\ 3/2}$ and $Ca_{2p\ 1/2}$ binding energies for the base-treated samples (347.2-347.5 eV) were lower than for the non-treated samples (349.8-350.1 eV). The lower binding energy observed for the treated coals is consistent with CaO while the higher energy of the non-treated coals is related to $CaSO_4$.

Molybdenum Analysis - The dual Mo_{3d} peaks were uniform for the Mo containing coals indicating that base-treatment had little effect on the bonding of the metal. The concentration of the metal was so small that no perturbation of the oxygen binding energy was observable. Quantification and characterization of Mo in the 500-1000 ppm range is difficult because it is close to the detection limit of XPS, even though the surface concentration is typically higher than the

bulk concentration. The S_{2s} peak overlaps with the Mo_{3d} peak measurement and is especially troublesome in samples having low concentrations of Mo and high concentrations of S. Pradhan, et al.,⁸ employed a peak subtraction method to resolve this problem. Although the Mo_{3d} peak in the Fe-Mo-impregnated coals is broadened, peak deconvolution was performed based upon external standards and knowing the S_{2s} and Mo_{3d} peak positions and the relative intensities of the S_{2p} peak (169-171 eV), which is quite intense, and the S_{2s} peak. Standards were provided by Mo, Ni and W impregnated sulfated iron oxide samples. The S_{2s} and S_{2p} peak positions for SO_4^{2-} were at 169.5 eV and 232.6 eV, respectively. The relative intensity ratio of S_{2s}/S_{2p} was 0.45-0.52. The $Mo_{3d\ 5/2}$ peak at 232.0 and $Mo_{3d\ 3/2}$ at 235.1 agree with those observed for the Fe-Mo-impregnated coals. Subtraction of the half-height S_{2p} peak area from the measured Mo_{3d} peak area provided a reliable method for determining Mo concentration.

Liquefaction Performance - The Fe- and Fe-Mo-impregnated coals gave significantly higher THF conversion and oil yields than raw coal when reacted in tetralin at 415°C, 1 hour, and 1000 psi H_2 cold. As-received coal gave 85 wt% THF conversion and 43 wt% oil yield; Fe-impregnated coals gave THF conversions of 88-90 wt% and oil yields of 45-50 wt%; Fe-Mo-impregnated coals gave THF conversions from 88-93 wt% and oil yields from 51-52 wt%. The use of iron sulfate salts without base-treatment appears to provide increased THF conversion and oil yield compared to metal impregnation with either sulfate or nitrate salts followed by base-treatment.

- Conclusions** - 1. Fe concentrations on the surface of Mo-free coals, impregnated with either Fe^{++} or Fe^{+++} sulfates, were lower than obtained with Fe^{+++} nitrates.
 2. Fe concentrations on the surface of Mo-Fe-impregnated coals, whether prepared from sulfate or nitrate salts, were intermediate between the Mo-free sulfate and nitrate preparations.
 3. Fe on the surface of all of the sulfate-impregnated coals was not present as $FeOOH$, which was the dominant form for the nitrate-impregnated, base-treated coals.
 4. Mo was present on the surface of the coal as MoO_3 .
 5. Sulfate is removed from sulfate-treated coals during the base-treatment step.
 6. Sulfur, on the surface of the non-base-treated coals that were treated with sulfates, was present as SO_4^{2-} .
 7. Oxygen concentrations on the surface of all the 0.77 wt% Fe-impregnated coals fall within a narrow range.
 8. Si, Al and Ca concentrations on the surface of the base-treated coals tend to be lower than for the non-base-treated samples.

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Table 1. Surface Composition of Fe-Impregnated Coals ^a , wt%													
Number		CH-31	CH-51	CH-53	CH-503	CH-504	CH-52	CH-502	CH-501	CH-6	CH-61	CH-604	CH-601
Impregnating Salt ^b	none	FN	Fe ⁺³	Fe ⁺³	Fe ⁺³	Fe ⁺³	Fe ⁺²	Fe ⁺²	Fe ⁺²	FN-AM	FN-AM	Fe ⁺³ -AM	Fe ⁺² -AM
Added Fe, wt% dry coal	none	0.77	2.0	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.71	0.77	0.77
Precipitated ^c	-	Y	Y	Y	N	N	Y	N	N	Y	Y	N	N
Washing	-	N	Y	Y	N	N	Y	N	N	N	N	N	N
Drying @ 40°C	-	Vac	Vac	Vac	N ₂	Air	Vac	N ₂	Air	Vac	Vac	Air	Air
Fe	0.33	4.2	7.9	1.5	1.6	1.9	1.2	1.9	0.8	2.5	3.0	2.3	2.5
Mo, ppm wt	-	-	-	-	-	-	-	-	-	0.14	0.11	0.51	0.30
Carbon	71.1	62.4	50.9	67.9	63.3	57.1	66.3	57.1	60.9	62.8	63.9	56.3	58.7
Oxygen	20.6	24.8	30.6	23.1	23.2	26.6	23.2	26.6	25.6	24.4	24.4	25.5	25.3
Nitrogen	1.3	1.2	1.0	1.1	1.0	1.0	1.3	1.0	1.0	1.5	1.4	1.5	1.2
Silicon	4.0	3.3	4.2	2.5	4.3	5.0	4.1	5.0	5.7	3.8	2.8	5.9	5.3
Aluminum	2.0	2.5	4.3	2.6	3.4	4.6	2.6	4.6	4.1	3.5	3.4	5.5	4.9
Calcium	0.5	1.0	0.9	0.8	1.2	1.5	0.8	1.5	0.8	1.3	0.9	1.0	0.8
Sulfur	0.2	0.6	0.2	0.4	1.9	2.4	0.4	2.4	1.2	0.03	0.03	1.4	1.1

a. Starting coal as "as-received" coal b. FN=Fe(NO₃)₃•9H₂O ; F⁺³=Fe₂(SO₄)₃•5H₂O ; Fe⁺²=FeSO₄•7H₂O ; AM=Ammonium Molybdate
c. Precipitated with NH₄OH solution; Y=yes; N=no.

a. Starting coal as "as-received" coal b. FN=Fe(NO₃)₃•9H₂O ; F⁺³=Fe₂(SO₄)₃•5H₂O ; Fe⁺²=FeSO₄•7H₂O ; AM=Ammonium Molybdate
c. Precipitated with NH₄OH solution; Y=yes, N=no.

Table 2. Binding Energies of Elements in Fe and Fe-Mo Impregnated Coals

	Salt ¹	Base	Fe eV			O _{1s} eV	N _{1s} eV	Si _{2p} eV	Al _{2p} eV	C _{2p} eV		S _{2p} eV	Mo _{3d} eV	
			Fe _{2p 3/2}	Fe _{2p 1/2}	Fe _{3p}					C _{2p 3/2}	C _{2p 1/2}		Mo _{3d 3/2}	Mo _{3d 5/2}
CH-31	FN	Y	711.1	725.1	56.6	531.7	399.1	103.8	75.0	346.2	351.0	162.1 168.4	N.D.	N.D.
CH-51	Fe ⁺³	Y	711.3	725.1	56.6	531.7	399.5	N.D.	N.D.	N.D.	N.D.	163.3 167.0	N.D.	N.D.
CH-52	Fe ⁺²	Y	711.7	725.4	56.3	532.5	399.1	N.D.	N.D.	347.4	350.6	164.0 169.7	N.D.	N.D.
CH-53	Fe ⁺³	Y	711.5	725.6	56.2	532.4	400.0	103.6	N.D.	347.2	351.0	163.6 169.6 168.4	N.D.	N.D.
CH-501 ²	Fe ⁺²	N	710.5 711.8	727.5 725.9	54.1	532.9	400.2 396.6	104.5	76.1 74.2	349.9	353.1	163.2 171.2	N.D.	N.D.
CH-502	Fe ⁺²	N	710.0 711.4		55.6	532.6	399.8	104.1	75.6	349.8	353.3	163.3 171.1	N.D.	N.D.
CH-504	Fe ⁺³	N	710.9 711.4 711.9	726.6	56.4	532.7	400.7	104.1	75.4	350.1	353.9	163.6 171.5	N.D.	N.D.
CH-6	FN-AM	Y	711.3	724.8	56.1	532.2	399.6	103.0	74.8	N.D.	N.D.	164.8 169.2	232.4	235.9
CH-61	FN-AM	Y	711.3	725.1	56.0	532.0	399.8	N.D.	74.8	347.5	351.0	163 169	232.5	235.6
CH-601	Fe ⁺² -AM	N	709.8	727.4	53.5	532.6	400.1 392.3	104.0	73.3	349.9	354.0	164.3 171.2	232.5	235.4
CH-604	Fe ⁺³ -AM	N	710.5	727.6	55.4	532.6	399.5 394.1	104.1	73.7	N.D.	N.D.	163.0 170.9	232.3	235.4

N.D. = not detected

1. FN=Fe(NO₃)₃·9H₂O ; F⁺³=Fe₂(SO₄)₃·5H₂O ; Fe⁺²=FeSO₄·7H₂O ; AM=Ammonium Molybdate 2. CH-501 Fe_{3s}=93.8 and 96.0 eV.